Proceedings of the 11th International Conference on
Non-conventional Materials and Technologies (NOCMAT 2009)
6-9 September 2009, Bath, UK

INFLUENCE OF CARBONATION ON THE LOAD DEPENDANT DEFORMATION OF HYDRAULIC LIME MORTARS

Richard J Ball [1], Adel El-Turki [2], Geoffrey C Allen [3]

University of Bristol, Interface Analysis Centre

Abstract: The time dependant deformation of natural hydraulic lime mortar (NHL3.5) through creep and shrinkage under load has been investigated. An apparatus was constructed to measure the dimensional changes of eight individual specimens simultaneously. A reversible relationship between specimen strain and relative humidity has been established. The influence of load on deformation rate was found to decrease with time during the experiment. The rate of decrease in load dependant deformation, creep, with time was shown to be inversely proportional to the extent of carbonation. This observation was explained by changes in composition resulting from carbonation of calcium hydroxide.

Keywords: *Lime mortar, deformation, creep, shrinkage, Raman spectroscopy*

1 Introduction

In recent years the adoption of lime mortars for applications where Portland cement may have otherwise been used has increased (Allen et al. 2003 and Holmes and Wingate 2002). Temperatures of around 900 ^{o}C are employed for the manufacture of hydraulic limes which comprise of calcium hydroxide and dicalcium silicate. In comparison higher temperatures of 1400 ^{o}C are used in cement manufacture and result in the formation of dicalcium silicate, tricalcium silicate, tricalcium aluminate and calcium aluminoferrite clinkers. The main consequence of these compositional variations is that the setting time for a lime mortar is substantially longer than that of cement and highly dependant on the carbonation rate of calcium hydroxide (El-Turki et al. 2009, Lawrence 2006, and Van Balen 1994).

When designing any structure or building a detailed knowledge of the mechanical properties is essential to accurately predict behavior during the service life. In the case of cement and concrete, architects and engineers can reliably predict strengths after periods as short at a few weeks and optimize designs accordingly. However in lime structures, uncertainty over the exact environmental conditions to which the setting mortar may be exposed leaves a large window of performance for its mechanical properties.

Various researchers have investigated the creep behavior of mortars. Bazant (1999) reported criteria for the prediction of creep and shrinkage in concrete and the creep behavior of clay masonry has also been studied by Shrive et al. (1997). An extensive study of creep and shrinkage has been carried out by Sickels Taves (1995) on mortars used in restoration but the majority of these contained a proportion of cement.

[1] Researcher, richard.ball@bristol.ac.uk
[2] Researcher, a-el.turki@bristol.ac.uk
[3] Professor, g.c.allen@bristol.ac.uk

Previous research by the authors has identified load dependant (creep) and load independent (shrinkage) contributions to the deformation of lime mortars during the initial period of setting (Ball et al. 2009). Here we report an investigation of the way in which the shrinkage and creep components of deformation are affected by carbonation.

2 Experimental Method

2.1 Raw materials and specimen preparation

A 1:2 hydraulic lime (NHL3.5) to sand mortar was prepared using a Croxden sand as the aggregate from Staffordshire, UK, with the particle size distribution shown in figure 1. Its composition determined by energy dispersive x-ray analysis indicated the presence of silicon, aluminium, potassium, oxygen, iron, titanium and calcium in order of decreasing signal intensity (Ball et al. 2009). NHL3.5 was supplied by Hanson Cement, formerly Castle Cement Ltd, Clithero, UK. A water to lime ratio of 0.78 provided a mix flow between 180-200 mm as recommended by the manufacturer.

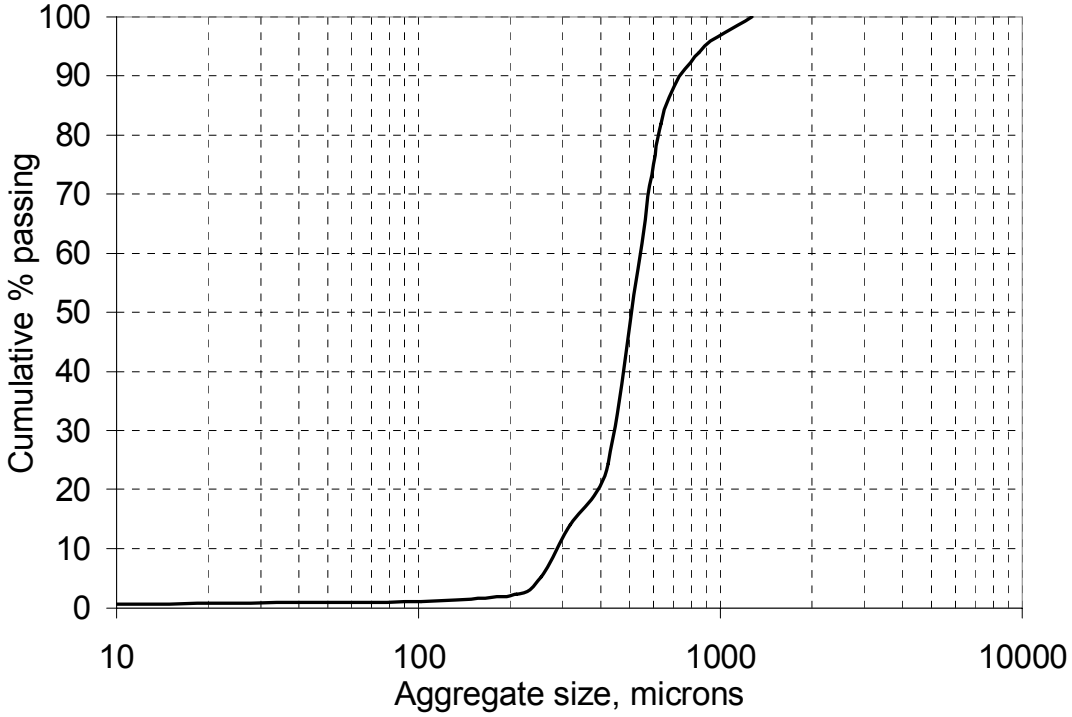

Figure 1: Croxden sand particle size distribution

The mortar was prepared by stirring the solid constituents prior to adding the water and mixing further. Cylinders 18 mm in diameter and 36 mm in length were cast in a pre-oiled mould. To ensure an even distribution of mortar and reduce the presence of air pockets within the specimens each mould was tapped repeatedly until no air bubbles were seen emerging from the surface. After 4 days the specimens were demoulded and a thin layer of high alumina cement applied to the top and bottom of each specimen to ensure flat and parallel end faces. The specimens were then left under the laboratory conditions of 19 ^{o}C and 47% relative humidity (RH) to harden.

2.2 Compressive testing

The compressive strength was determined using a 10 kN Zwick/Rowell testing machine. Each specimen was mounted between two parallel stainless steel platens. The

top platen was allowed to pivot on a ball joint to accommodate specimen surface irregularities. Loading was applied at a constant stress rate of 0.079 $Nmm^{-2}s^{-1}$ until the ultimate value was reached. Specimens were tested at ages of 7, 39 and 63 days from mixing. Tests at 39 and 63 days were carried out for both open and sealed specimens. This equated to 0, 32 and 56 days for the specimens in the deformation rig. Within this paper times quoted in the text and figures refer to the time in the deformation rig as opposed to the time from mixing.

2.3 Creep rig

The creep rig containing eight individual locations for simultaneous specimen monitoring was constructed as shown in figure 2. Displacements were logged using a PC interfaced with Solartron Metrology linear displacement transducers via an Orbit Measurement System to an accuracy of 50 nm. Readings were recorded at intervals of 10 seconds.

The pivot points within the creep rig were required to operate under a high load in conjunction with exceptionally low rotational displacements related to the specimen deformation. Within such a machine it was important to ensure that binding of the pivots did not result in fluctuations in the load applied to the specimen over time. The rig was commissioned, using an Omegadyne Inc LCM703-250 load cell connected to a PC with an interface and data logging software, by monitoring force and resulting displacement applied to a small cube of lead approximately 10x10x10 mm over a period of 10 days. The force remained constant with changing displacement.

Following an initial seven day post-mixing period of hardening, eight specimens were inserted into the creep rig. Four of these were coated with a layer of petroleum jelly to restrict the diffusion of carbon dioxide and water vapour into and out of the specimen. Coated specimens are referred to as ‘sealed’ and uncoated specimens as ‘open’. Details of the loads applied to the specimens are given in table 1. Where no load was applied to the end of the arm the respective specimens experienced the weight of the arm. This minimal load was necessary to ensure good contact between the loading platens and specimen surfaces.

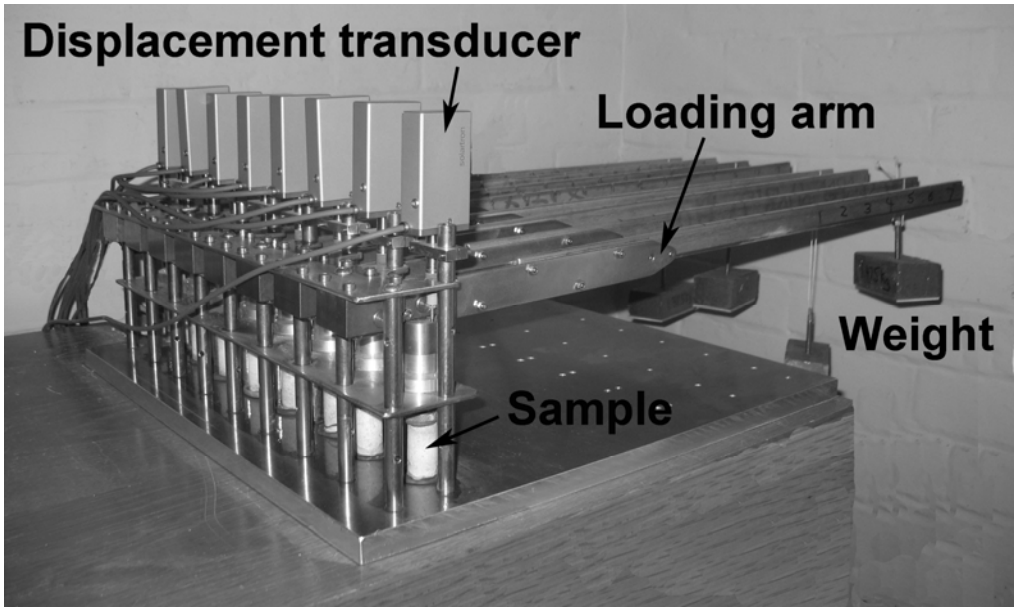

Figure 2: Photograph of rig used to monitor shrinkage and creep

Table 1: Loads applied to specimens monitored in deformation rig

Specimen number	***Coated with petroleum jelly***	***Load applied to specimen (MPa)***
1 (open)	No	0.92
2 (open)	No	0
3 (open)	No	0.95
4(open)	No	0
5 (sealed)	Yes	0.92
6 (sealed)	Yes	0
7 (sealed)	Yes	1.02
8 (sealed)	Yes	0

2.5 Raman spectroscopy

Specimen materials were characterised using a Renishaw Ramascope spectrometer model 2000. The system was equipped with an Ar^+ laser as an excitation source operating at a wavelength of 488 nm and maximum laser power of 25 mW. The analyses were performed by focusing the laser with objective magnification x50 onto the specimen surface through an Olympus BH2-UMA optical microscope, corresponding to a laser spot diameter of about 4μm. The laser power at the specimen surface was of the order of 3mW and an acquisition time of 10 seconds was used for each spectrum over the wavenumber range 100-4000 cm^{-1}. Prior to the analysis, the spectrometer was calibrated using a monocrystalline silicon standard specimen. Peak fitting and deconvolution of Raman spectra were performed using GRAMS32 software.

3 RESULTS AND DISCUSSION

3.1 Effect of relative humidity on deformation

The temperature and RH were monitored over the duration of the experiment. An average temperature of 19.2 ^oC and relative humidity of 46.9 % with standard deviations of 1.9 ºC and 3.4 % respectively were recorded. Perturbations in RH correlated with changes in the observed deformation, suggesting a relationship between these parameters. Figure 3 shows plots of strain and relative humidity versus time between 20 and 56 days, note the strain axis is reversed. An increase in strain corresponds to an increase in relative humidity between 20 and 42 days. At this juncture a rapid drop in relative humidity corresponds to a decrease in strain. A lag is observed between the change in relative humidity and strain. This is believed to be a function of the time taken for water to diffuse into the sample. The average strains per 1% change in RH for sealed specimens with and without load applied were $2.9x10^{-5}$ and $3.0x10^{-5}$ respectively indicating no significant difference. In comparison the open specimens exhibited strains per 1 % change in RH of $3.9x10^{-5}$ and $5.1x10^{-5}$ for specimens with and without load applied respectively. The larger strains per 1 % change in RH recorded for the open specimens were attributed to the ability of water vapor to diffuse in and out of the specimens. When comparing the open specimens the greater strains measured for the specimen with no load applied indicates that the strain was load dependant.

3.2 Compressive strengths and phenolphthalein staining

The initial compressive strength of the specimens was 1.5 MPa. The strength of the open samples increased to 1.8 and 1.9 MPa at 32 and 56 days respectively. Lower

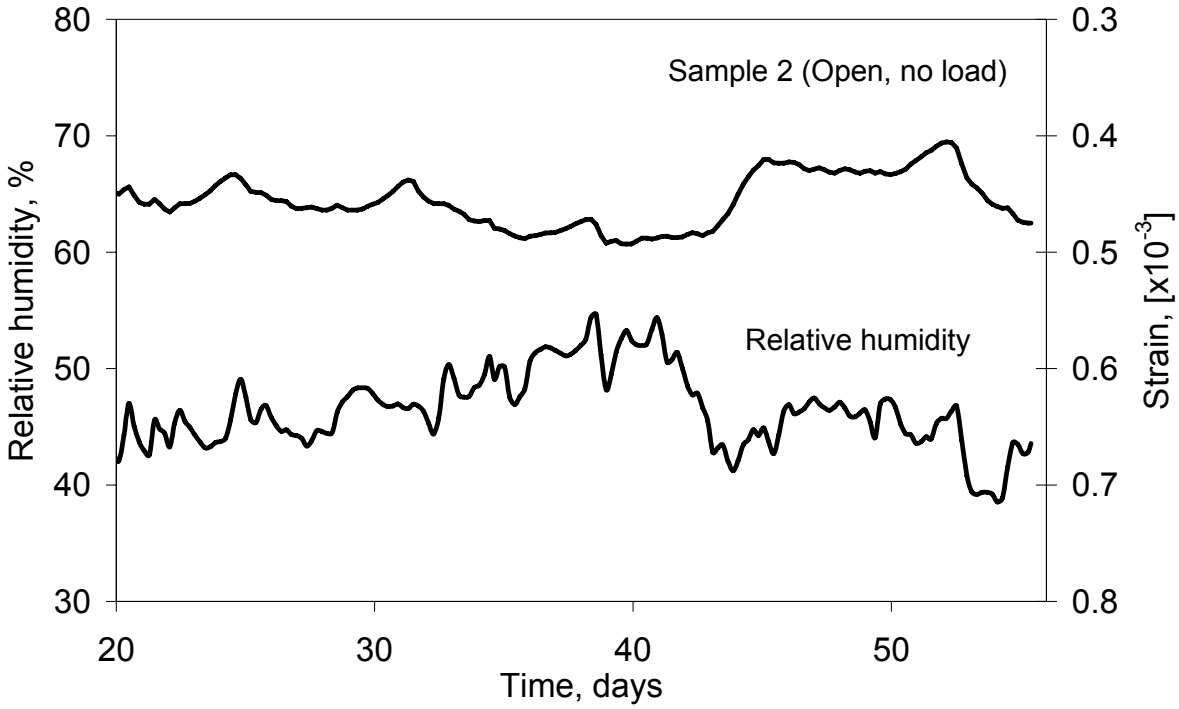

Figure 3: Plots of strain and relative humidity versus time between 20 and 56 days.

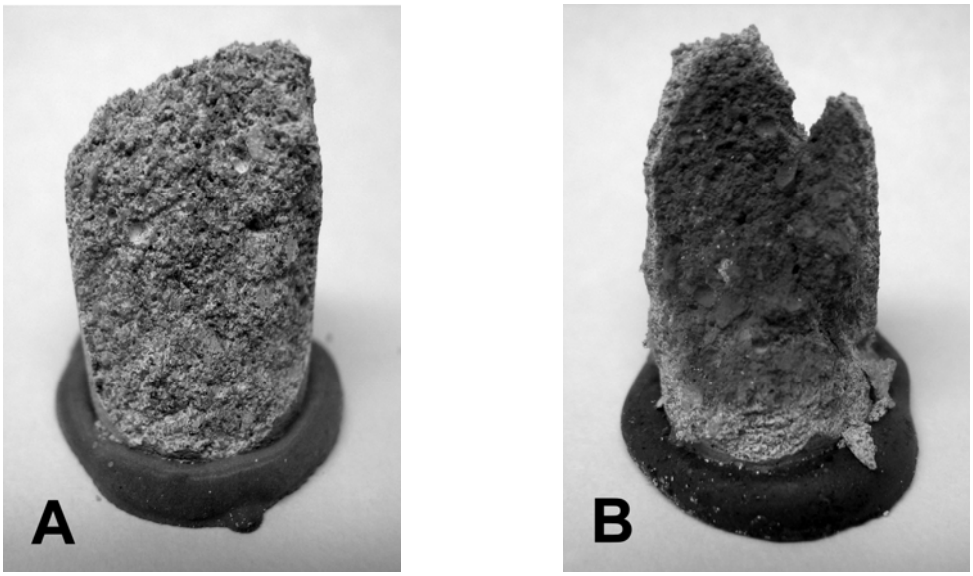

Figure 4: Phenolphthalein stained cross sections of NHL3.5 lime mortar. (A) open (B) sealed. The greater intensity in the sealed specimen indicated that less carbonation had occurred compared to the open specimen.

strengths of 1.5 and 1.8 MPa were recorded at 32 and 56 days respectively for the sealed samples. Figures 4 (A) and (B) show fracture surfaces of open and sealed specimens at 56 days which were stained using a saturated solution of phenolphthalein indicator in ethanol. A more intense staining was observed within the sealed specimen indicating a higher proportion of calcium hydroxide.

3.3 Deformation of NHL3.5 lime mortar

The deformation of the mortar was monitored over a period of 56 days. Following an initial period when there was a relatively large change, the deformation rate was observed to decrease reaching a steady value. Creep is defined as the time dependant deformation of a specimen under load therefore the difference between the strain rates in the loaded and unloaded specimens represented the creep rate. This is illustrated for the open and sealed conditions in Figure 5.

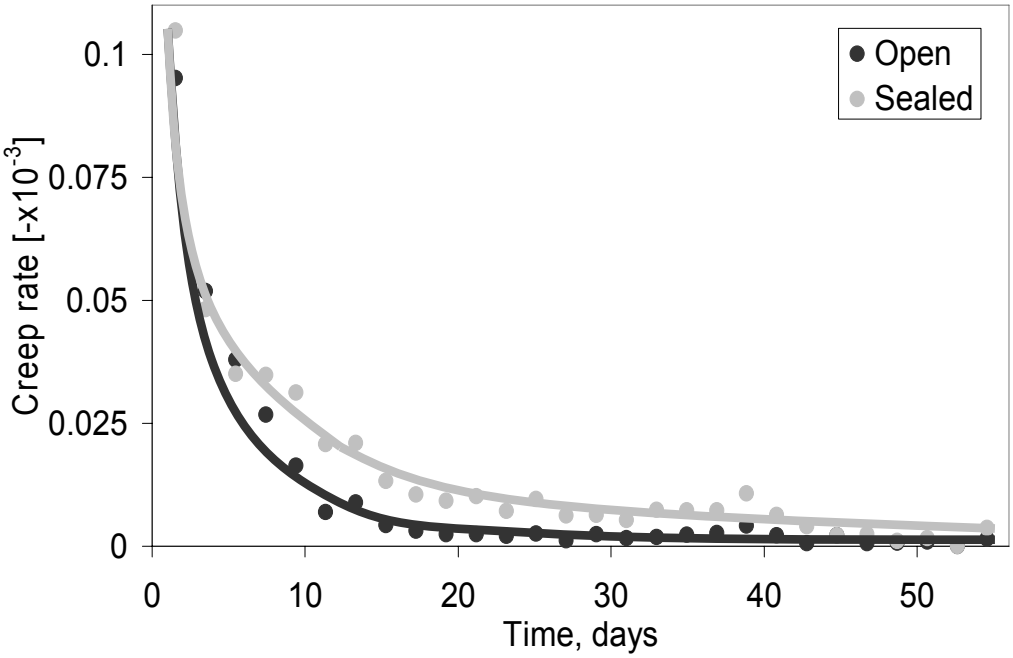

Figure 5: Load dependant deformation for open and sealed specimens.

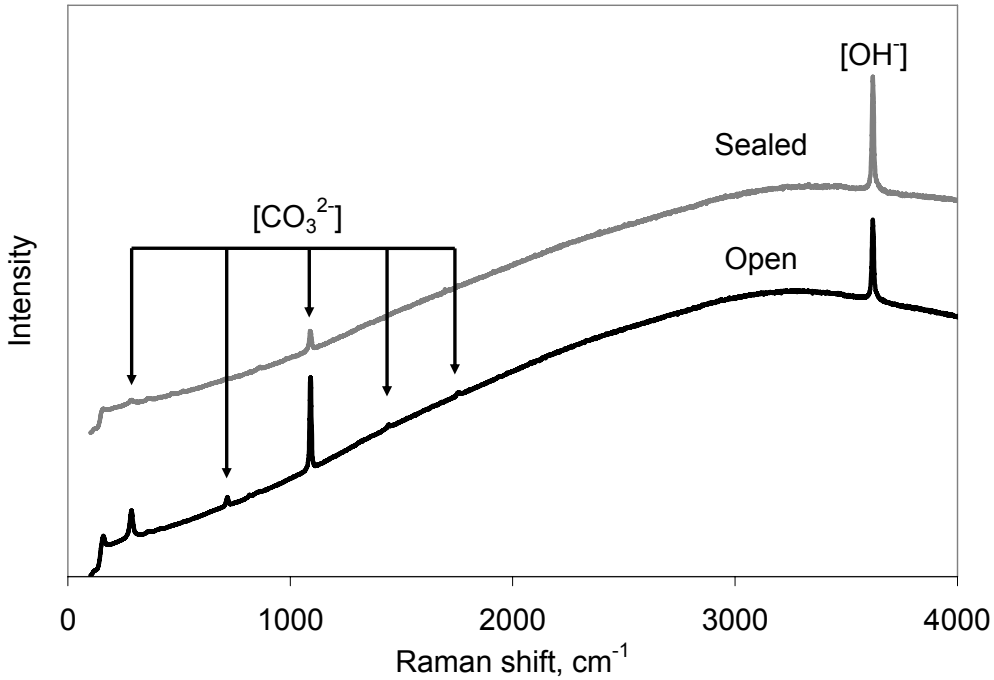

Figure 6: Raman spectra of sealed and open specimens after 56 days.

3.4 Raman spectroscopy

Raman spectra recorded from a fracture surface of open and sealed mortar specimens are shown in figure 6. Vibrational modes of the free CO_3^{2-} ion in calcium carbonate at 1085, 712 and 280 cm^{-1} were identified. These correspond to the v_1, v_4, and ($v_3 - v_1$) vibrations respectively. Of these v_1 is the strongest. An additional two weaker asymmetric stretching v_3 bands located at 1436 and 1746 cm^{-1} were also present. The spectrum of calcite is in agreement with that reported previously by Rutt and Nicola (1974). In addition to these bands, a strong band at 3614 cm^{-1} is attributed to the main symmetrical stretching vibration mode for the OH^- group in calcium hydroxide (Baranek *et al* 2001 and Kwon *et al* 2004). Consideration of the relative intensities of these bands gives an indication of the relative proportions of the phases present. The band corresponding to the OH^- in calcium hydroxide was strongest in the sealed specimens and the v_1 band corresponding to the CO_3^{2-} in calcium carbonate was strongest in the open specimen. This indicated that the petroleum jelly used to seal the specimens was effective in restricting the formation of calcium carbonate in comparison to the open specimens.

4 Discussion

The creep response measured for the specimens tested was similar to that observed previously, the curve can be divided into different stages. The first stage, up to approximately two days, corresponded to bedding – in of the sample as asperities on the sample surface were flattened by the smooth loading platens. Following this period a deformation in the form of two stages, primary and secondary creep, was identified. Primary creep was attributed to load dependant, creep, and load independent deformation, shrinkage, while secondary creep corresponded to shrinkage. In previous studies primary creep was observed to last approximately 14 days (Ball et al 2009). A similar duration was observed in this study for the open specimens but a longer period was required for the sealed specimens. This observation is clearly shown by comparing the gradients of the curves in figure 5. In these specimens tertiary creep, a phenomenon used to describe the point to failure, was not observed and would have been unlikely to occur where there was no increase in stress. Moreover the observed deformation took the general form normally recorded for strain-time curves used to describe materials subject to creep (Mindness 1981, Neville 1970). It should be noted that the absence of tertiary creep did not imply that the specimens could not fail by brittle fracture.

The structure of a mortar can be represented as a slightly porous composite comprising sand particles surrounded by a lime matrix. Such structures do not generally exhibit significant creep processes within the time scales or loads employed in the current study. However the sand particles by their very nature possess high stiffness and it is therefore reasonable to assume that any creep or shrinkage observed would be accommodated solely by the softer lime matrix.

Hydraulic limes harden by hydration and carbonation reactions, processes associated with chemical structural changes within the matrix. Under load, reconfiguration of individual crystals would be associated with a corresponding change in sample dimension. Therefore it is suggested that carbonation reduces the rate of creep, and that the extent of carbonation controls the rate of load dependant creep deformation observed.

It is interesting to compare the absolute amount of creep. As suggested in figure 5 the uncarbonated specimens suffered a greater absolute amount of creep strain, 0.95×10^{-3}, compared to the carbonated specimens which suffered a lesser creep strain of 0.64×10^{-3}.

5 Conclusions

The following conclusions have been drawn from the results presented.

- Time dependant deformation was observed in 1:2 NHL3.5 lime / sand mortars. This was attributed to a creep mechanism which is load dependant and a shrinkage mechanism which is independent of load. The load dependant creep component was most significant during the fourteen days after insertion into the rig.
- The load dependant component of deformation in a NHL3.5 lime mortar, creep, was dependant on the extent of carbonation. Sealed specimens with corresponding lower carbonation rates required a longer period of time for the creep component to reduce.

6 Acknowledgements

The authors would like to thank Castle Cement for supplying the raw materials.

7 References

ALLEN, G.C., ALLEN, J., ELTON, N., FAREY M., HOLMES S., LIVESEY P. AND RADONJIC M., 2003. *Hydraulic lime mortars for stone, brick and block masonry*, Shaftsbury: Donhead Publishing.

BALL R.J., EL-TURKI A., ALLEN, W. J., NICHOLSON J. A. AND ALLEN, G. C., 2009. Deformation of NHL3.5 and CL90/PC hybrid mortars, *Construction Materials. Proceedings of the Institute of Civil Engineering*, 162(CM2), pp.29-35.

BAŽANT, Z.P., 1999. Criteria for rational prediction of creep and shrinkage of concrete, *Rev. Française Génie Civil,* 3(3/4), pp.61–89.

BARANEK, P.H., LICHANOT, A. ORLANDO, R. AND DOVESI R., 2001. Structural and vibrational properties of solid $Mg(OH)_2$ and $Ca(OH)_2$ - Performances of various Hamiltonians. *Chemical Physics Letters,* 340(3/4), pp.362-369.

EL-TURKI, A., CARTER, M.A., WILSON, M.A., BALL, R.J. AND ALLEN G.C., 2009. A microbalance study of the effects of hydraulicity and sand grain size on carbonation of lime and cement. *Construction and Building Materials*, 23, pp.1423-1428.

HOLMES S. AND WINGATE M., 2002. *Building with lime, a practical introduction (revised edition).* London: ITDG Publishing.

KWON, T.Y., FUJISHIMA T. AND IMAI Y., 2004. FT-Raman spectroscopy of calcium hydroxide medicament in root canals. *International Endodontic Journal*, 37, pp.489-493.

LAWRENCE, R.M.H., MAYS, T.J., WALKER P. AND D'AYALA, D. 2006. Determination of carbonation profiles in non-hydraulic lime mortars using thermogravimetric analysis *Thermochimica Acta,* 444(2), pp.179-189.

MINDNESS, S. AND YOUNG, J. F., 1981. *Concrete.* New Jersey: Prentice-Hall, Inc.

NEVILLE, A. M., 1970. *Creep of concrete: plain, reinforced, and prestressed*. Amsterdam: North-Holland Publishing Company.

RUTT, H.N. and NICOLA, J.H., 1974. Raman spectra of carbonates of calcite structure, *Journal of Physical Chemistry C: Solid State Physics*, 7, pp.4522-4528.

SHRIVE, N.G., SAYED-AHMED, E. AND TILLEMAN, D. 1997. Creep analysis of clay masonry assemblages. *Canadian Journal of Civil Engineering*, 24(3), pp.367–379.

SICKELS TAVES L.B., 1995. Creep, shrinkage and mortars in historic preservation. *Journal of Testing and Evaluation.* 23, pp.447–452.

VAN BALEN, K. AND VAN GEMERT, D., 1994. Modelling lime mortar carbonation. *Materials and Structures*, 27(171) pp.393-398